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# Inverse modeling of the biodegradation of emerging organic contaminants in the soil-plant system

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## Abstract

Understanding the processes involved in the uptake and accumulation of organic contaminants into plants is very important to assess the possible human risk associated with. Biodegradation of emerging contaminants in plants has been observed, but kinetical studies are rare. In this study, we analyse experimental data on the uptake of emerging organic contaminants into lettuce derived in a greenhouse experiment. Measured soil, root and leaf concentrations from four contaminants were selected within the applicability domain of a steady-state two-compartment standard plant uptake model: bisphenol A (BPA), carbamazepine (CBZ), triclosan (TCS) and caffeine (CAF). The model overestimated concentrations in most cases, when no degradation rates in plants were entered. Subsequently, biodegradation rates were fitted so that the measured concentrations were met.

Obtained degradation kinetics are in the order, BPA < CAF ≈ TCS < CBZ in roots, and BPA ≈ TCS < CBZ << CAF in leaves. Kinetics determined by inverse modeling are, despite the inherent uncertainty, indicative of the dissipation rates. The advantage of the procedure that is additional knowledge can be gained from existing experimental data. Dissipation kinetics found via inverse modeling is not a conclusive proof for biodegradation and confirmation by experimental studies is needed.

**Keywords**: dissipation; kinetics; plants; model; emerging organic contaminants.

## 1. Introduction

Pharmaceuticals, biocides and drugs as well as other chemicals from human use reach sewer systems and are partially removed during conventional wastewater treatment processes (Halling-Sørensen et al., 1998). By irrigation with reclaimed water, or sewage sludge amendment, these chemical residues may reach agricultural soils. Uptake into crops can lead to human exposure to such chemicals (Hospido et al., 2010). In the European Union, the environmental risk from pharmaceutical products is assessed only for veterinary drugs (EMA, 2011), and only few pharmaceuticals and drugs are regularly monitored according with the Watch List of the Water Framework Directive (Directive 2008/105/EC). Then, human exposure to emerging organic contaminants (EOCs) relies partly on scientific studies, and an increasing number of studies on their uptake into vegetables is reported (Wu et al., 2015; Miller et al., 2016).

Prosser and Sibley (2015) found no human health hazards from the plant uptake of the “majority of pharmaceuticals and personal care products”. However, Malchi et al. (2015) stated that “current data are insufficient to support a comprehensive human health risk assessment” of pharmaceuticals and personal care products in plant tissue due to biosolids and manure amendments, or reclaimed water irrigation. Due to the high number of compounds potentially present in reclaimed water (Calderón-Preciado et al., 2011; Loos et al., 2013; Luo et al., 2014), prediction tools for pre-screening of chemicals and priority setting for safety assessments are of high value (Polesel et al., 2015). Prosser et al. (2014) examined the ability of two prediction models to estimate the uptake of

59 pharmaceuticals and personal care products (PPCPs) into plants from sludge-
60 amended soils. Predictions of plant uptake of PPCPs within one order of
61 magnitude near the experimental results were achieved for some of the
62 investigated compounds. Polesel et al. (2015) developed and tested a simulation
63 tool for fate prediction from human pharmaceuticals down the drain through a
64 sewage treatment plant and via sludge amendment and irrigation to agricultural
65 fields and crops. However, simulations were performed disregarding degradation in
66 plants. To reduce discrepancies between model predictions and measurements,
67 the authors stressed the need for more measured input parameters (e.g., $K_d$) and
68 kinetics of biotransformation in plant tissues.

69 For polar compounds, efficient translocation in xylem of plants can be expected
70 (Trapp, 2007; Dettenmaier et al., 2009), leading to accumulation in leaves, if no
71 losses occur. Biodegradation has been identified as among the most relevant
72 dissipation processes of chemicals from plants (Fantke et al., 2012; Jacobsen et
73 al., 2015), but is often unknown or uncertain and depends on a number of factors,
74 such as species and temperature (Fantke and Juraske, 2013; Fantke et al., 2014;
75 Jacobsen et al., 2015). Methods to measure metabolism in soil and plants have
76 been developed early, typically employing the use of $^{14}$C-labeled compounds to
77 close the mass balance (Trapp et al., 1990; Kästner et al., 2014). There are also
78 OECD guidelines for pesticide metabolism in crops to elucidate the degradation
79 pathway available (i.e. OECD Tests Nr. 501, 502). The drawback is that studies
80 with hot labels are expensive, and safety issues arise. These safety issues can be

81 solved by using stable isotopes ($^{13}C$ and $^{15}N$), but require IRM-MS equipment, if
82 isotopically labeled compounds are available at all.

83 An alternative method to assess biodegradation that has rarely been attempted is
84 the use of inverse modeling. Hereby, predictable loss due to physical-chemical
85 processes (volatilization, translocation, dilution) is contrasted with measured
86 dissipation. The difference is contributed to biodegradation. This method cannot
87 prove degradation but can help to quantify loss processes (Jacobsen et al., 2015).

88 The kinetics of biodegradation affects the relation between concentrations in plants
89 and soil. First-order degradation kinetics, either in soil or in plants, will change the
90 slope of the trend line (lower for degradation in plants, higher for degradation in
91 soil), but the relation will remain linear. In a study with lettuce grown under
92 controlled conditions and irrigated with water containing eight emerging organic
93 contaminants (EOCs), Hurtado et al. (2016) obtained mostly linear correlations
94 between watering concentrations and concentrations measured in roots and
95 leaves. Besides hydrophobicity (log $D_{OW}$) of chemicals, their persistence was
96 identified as a key determinant for plant uptake and accumulation of the EOCs.

97 In this study, we supplemented a standard plant uptake model (Rein et al., 2011)
98 with different degradation kinetics for soil and plant. The model was parameterized
99 to simulate the uptake experiments of emerging organic contaminants into lettuce
100 performed by Hurtado et al. (2016). Degradation rate constants in soil were derived
101 from the measured concentrations, while rates in leaves and roots were fitted,

based on the difference between the model prediction (without degradation) and the measured data. The resulting rates were compared to data from literature.

## 2. Materials and methods

### 2.1. Experimental section

Experiments were conducted in a glass greenhouse located in Viladecans (Barcelona, Spain) as described in Hurtado et al. (2016). Briefly, lettuce (*Lactuca sativa*) was planted in pots in a mixture of perlite and sand (2:1 v/v, approx. 1.2 kg) and watered with Hoagland nutrient solution (Hoagland and Arnon, 1950) diluted 1:1 with rain water. A dose of 50 mL of irrigation water was applied to each experimental unit per day. The number of daily irrigations was regulated to keep water in the soil below field capacity, thereby preventing leachate production.

After 40 days, EOCs were added to soil. Five treatments consisted of direct application of 0, 14, 35, 70 and 140 µg of eight EOCs per experimental unit in eight applications during 28 days. Taking into account the soil substrate mass in each experimental unit, this corresponds to an average nominal initial concentration in the substrate of 0, 11.7, 29.2, 58.3 and 116.7 µg $kg^{-1}$ dw. After 28 days, substrate, roots and leaves of lettuces were separated and analyzed. The data used in this study can be found in the SI and are also reported in Hurtado et al. (2016).

The EOCs measured in the experimental study were bisphenol A, caffeine, carbamazepine, ibuprofen, propranolol, sulfamethazine, triclosan and tonalide. All chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA), except

tonalide from Ventós (Sant Just Desvern, Spain). The extraction of EOCs from vegetal tissue and substrate and the analytical parameters are listed in Hurtado et al. (2016). The properties of the compounds are listed in Table 1.

**Table 1.** Properties of the compounds added in the experiment by Hurtado et al. (2016). All values were obtained using ACD Advanced Chemistry Development (2010), ACD/i-lab 2.0. Toronto, 2010.

| EOC | Molar mass (g $mol^{-1}$) | p*K*a values | Speciation (z) | Neutral log $K_{OW}$ | log $D_{OW}$ at pH 6.4 | log $K_{AW}$ | log $K_{HSA}$ |
|---|---|---|---|---|---|---|---|
| Bisphenol A (BPA) | 228.29 | 9.7, 10.5 | 0/-1/-2 | 3.46 | 3.46 | -9.43 | 3.57 |
| Caffeine (CAF) | 194.19 | NA | 0 | 0.11 | 0.11 | -8.83 | 2.53 |
| Carbamazepine (CBZ) | 236.27 | NA | 0 | 2.23 | 2.23 | -7.20 | 3.74 |
| Ibuprofen (IBU) | 206.28 | 4.3 | 0/-1 | 3.63 | 1.53 | -5.21 | 4.42 |
| Propranolol (PROP) | 259.34 | 9.5 | 1/0 | 2.69 | 0.13 | -10.49 | 3.54 |
| Sulfamethazine (SMT) | 278.33 | 3.1, 7.2 | 1/0/-1 | 0.31 | 0.25 | -11.33 | 4.1 |
| Tonalide (TON) | 258.40 | NA | 0 | 5.71 | 5.71 | -2.04 | 4.71 |
| Triclosan (TCS) | 289.54 | 8.8 | 0/-1 | 5.21 | 5.21 | -4.08 | 4.81 |

NA: Not applicable; z is charge number (valence); $K_{OW}$ (L $L^{-1}$) is the partition coefficient octanol to water for the neutral molecule; $D_{OW}$ (L $L^{-1}$) is the apparent partition coefficient of the neutral and ionic molecules at pH 6.4 (soil pH); $K_{AW}$ (L $L^{-1}$) is the partition coefficient air to water for neutral molecules (known as dimensionless Henry's Law constant) and $K_{HSA}$ (L $mol^{-1}$) is the adsorption to human serum albumin (as predictor for the adsorption to proteins).

## 2.2. Model section

The plant uptake model is based on the commonly used "standard model" for plant uptake (Legind and Trapp, 2009; Legind et al., 2011; Rein et al., 2011; Trapp,

2015). Modifications were introduced to consider different degradation kinetics. This version of the model is primarily designed for neutral compounds. As long as the fraction of ionic molecules is small, ionization only slightly affects the outcome when measured $K_d$-values are used. PROP, IBU and SMT were not included in the plant uptake simulations because the ionization prohibits the use of this model version. TON was excluded because of its high volatility. In a separate approach, *Michaelis-Menten* degradation kinetics in roots and leaves was calculated, but for mathematical reasons with initial (constant) concentration in soil.

The underlying differential equation for the change of concentration in roots ($C_R$, mg kg$^{-1}$) with time $t$ (d) is

+ inflow from soil - translocation upwards - dilution by growth - degradation

$$\frac{dC_R}{dt} = \frac{Q}{M_R} \times \frac{C_S}{K_d} - \frac{Q}{M_R \times K_{RW}} \times C_R - k_{growth} \times C_R - degradation \quad (1)$$

where $R$ is index for roots, $Q$ is the transpiration (L d$^{-1}$), $M$ is the plant mass (kg), $C_S$ is the concentration of chemical in soil (mg kg$^{-1}$), $K_d$ is the distribution coefficient between substrate and pore water (L kg$^{-1}$), $K_{RW}$ is partition coefficient roots to water (and xylem sap) (L kg$^{-1}$), and $k_{growth,R}$ is the growth rate of roots (d$^{-1}$).

The differential equation for the change of concentration in leaves ($C_L$, mg kg$^{-1}$) with time, neglecting uptake of chemical from air, is

+ translocation from roots - loss to air - dilution by growth - degradation

159 $$\frac{dC_L}{dt} = \frac{Q}{M_L \times K_{RW}} \times C_R - \frac{A_L \times g \times 1000\, L\, m^{-3}}{K_{LA} \times M_L} \times C_L - k_{growth,L} \times C_L - degradation \quad (2)$$

160 where *L* is index for leaves, *A* is area ($m^2$), g is conductance (m $d^{-1}$) and $K_{LA}$ is
161 partition coefficient between leaves and air (L $kg^{-1}$).

162

163 *a) Coupled dynamic differential equation system with first-order degradation*

164 The concentrations in soil, roots and shoots are calculated from a system of
165 coupled ordinary differential equations that form a triangular matrix and are solved
166 analytically.

167 The concentration in soil is considered time-dependent, with

168 $$C_S(t) = C_S(0) \times e^{-k_1 t} \quad (3)$$

169 The loss rate from soil $k_1$ (matrix element 1) was calculated from the measured
170 initial and final concentrations at time *t*, $C_S(t)$, assuming first-order loss due to
171 degradation, plant uptake and volatilization:

172 $$k_1 = \frac{\ln C_S(0) \big/ C_S(t)}{t} \quad (4)$$

173 The transfer rate from soil to roots is

174 $$k_{12} = \frac{Q}{M_R K_d} \quad (5)$$

175 The rate $k_2$ is the sum of all loss terms (to shoots, dilution, degradation) from roots
176 ($d^{-1}$)

177 $$k_2 = \frac{Q}{M_R \times K_{RW}} + k_{growth,R} + k_R \quad (6)$$

178 $k_R$ is the 1st order degradation rate that is to be fitted.

179 The rate $k_3$ ($d^{-1}$) is the sum of all loss terms (to air, dilution, degradation) from
180 leaves

181 $$k_3 = \frac{A_L \times g \times 1000\, L\, m^{-3}}{K_{LA} \times M_L} + k_{growth,L} + k_L \quad (6)$$

182 $k_L$ is the 1st order degradation rate that is to be fitted.

183 The transfer rate from roots to leaves is

184 $$k_{23} = \frac{Q}{M_L K_{RW}} \quad (7)$$

185 The analytical solution for the concentration in roots (matrix element 2) is

186 $$C_R(t) = \frac{k_{12} \times C_S(0)}{k_2 - k_1} \times \left(e^{-k_1 \times t} - e^{-k_2 \times t}\right) \quad (8)$$

187 and for leaves (matrix element 3) is

188 $$C_L(t) = k_{12} k_{23} C_S(0) \left\{ \frac{e^{-k_1 t}}{(k_2 - k_1)(k_3 - k_1)} + \frac{e^{-k_2 t}}{(k_1 - k_2)(k_3 - k_2)} + \frac{e^{-k_3 t}}{(k_1 - k_3)(k_2 - k_3)} \right\} \quad (9)$$

189 This model resembles the cascade model presented and tested by Rein et al.
190 (2011) and applied by Legind et al. (2011) and Prosser et al. (2014).

191

192 b) *Michaelis-Menten degradation kinetics in roots and leaves*

193 Enzymatic reactions often follow the *Michaelis-Menten* kinetics

194 $$degradation = \frac{v_{max} \times C}{K_M + C} \quad (10)$$

195 where $v_{max}$ is the maximal enzymatic removal in roots or leaves (mg $kg^{-1}$ $d^{-1}$) and
196 $K_M$ (mg $kg^{-1}$) is the concentration at which removal is half $v_{max}$. With *Michaelis-*
197 *Menten* type kinetics, the shape of the trendline between concentrations in soil and
198 plant is no longer linear. This kinetics has been observed for the degradation of
199 cyanide by plants (Larsen et al., 2004; Yu et al., 2004) and for the exclusion of salt
200 NaCl and NaF from roots (Trapp et al., 2008; Clausen et al., 2015). The
201 assumption of steady-state was made to allow for a closed analytical solution, and
202 requires constant concentration in soil $C_S(0)$. The steady-state leads to a quadratic
203 equation which was solved using Vieta's formulas (Larsen et al., 2004; Trapp et al.,
204 2008).

205 The comparison of experimental values from different studies with different
206 concentration levels is done by calculation of root concentration factor (RCF) and
207 leaf concentration factor (LCF) which are defined as

208 $$RCF = \frac{C_R(t_2)}{C_S(t_1)} \quad (11)$$

$$LCF = \frac{C_L(t_2)}{C_S(t_1)} \quad (12)$$

Here, $t_1$ and $t_2$ stand for the time when the concentrations were measured. While $t_2$ (the time when the concentration in root and leaf is determined) typically refers to the time of harvest, there is no standard for $t_1$, and initial, nominal or final (at harvest) concentrations have been used for the calculation of RCF and LCF.

*Model input data*

Where available, input data for the plant properties were taken from the experiment. As shown recently, plant properties can significantly affect the outcome of the model simulations (Trapp, 2015). The experiment was carried out in a greenhouse in Spain, but in the winter period. Growth was moderate (growth rate 0.05 $d^{-1}$), and the ratio of transpiration to plant mass was relatively low (Table 2).

**Table 2.** Input data for the simulation of the uptake experiment with lettuce. Data shown are for an individual pot. Displayed is the data set for an experiment with carbamazepine (experiment number 17). Data source Hurtado et al. (2016)

| | **Symbol** | **value** | **unit** | **Comment** |
|---|---|---|---|---|
| distribution coefficient | $K_d$ | 0.72 | L $kg^{-1}$ | measured |
| total loss rate | $k_1$ | 0.0895 | $d^{-1}$ | calculated from measurements |
| water content roots | $W_R$ | 0.898 | L $kg^{-1}$ | measured |
| lipid content roots | $L_R$ | 0.025 | kg $kg^{-1}$ | default |

| | | | | |
|---|---|---|---|---|
| mass of roots | $M_R$ | 0.0833 | kg | measured |
| transpiration | $Q$ | 0.053 | L $d^{-1}$ | calculated from added water |
| growth rate root | $k_{growth,R}$ | 0.05 | $d^{-1}$ | calculated from measurements |
| shoot mass | $M_L$ | 0.2227 | kg | measured |
| leaf area | $A$ | 1 | $m^2$ | default |
| conductance | $g$ | 0.001 | m $s^{-1}$ | default |
| lipid content leaves | $L_L$ | 0.02 | g $g^{-1}$ | default |
| water content leaves | $W_L$ | 0.954 | g $g^{-1}$ | measured |
| time between dosing and harvest | $t$ | 28 | d | measured |
| growth rate shoots | $k_{growth,L}$ | 0.05 | $d^{-1}$ | calculated from measurements |

## 3. Results

Dry weight and water content of substrate, root and leaf for the different experimental units can be found in Table S1. Final concentrations in the three compartments can be found in Tables S2, S3 and S4.

*Bioconcentration Factors derived from experimental data with lettuce*

Root concentration factor (RCF, kg $kg^{-1}$ dw) and leaf concentration factor (LCF, kg $kg^{-1}$ dw) were calculated as the slopes of the linear regression of the concentration in plant versus either the initial (nominal) or the final concentration in the soil substrate. Figure 1 shows the RCFs and LCFs of CBZ and IBU. RCFs obtained for

CBZ were rather similar when initial or final concentrations of CBZ in soil were used to establish the regression. The slope, interpreted as RCF, was 10.4 kg $kg^{-1}$ dw with the initial and 9.6 kg $kg^{-1}$ dw with the final substrate concentration, however, the y-intercept went from -45 µg $kg^{-1}$ dw to +92 µg $kg^{-1}$ dw. Also the LCF of CBZ changed very little, from 17.6 to 15.1 kg $kg^{-1}$ dw (but with high Y-intercept of 268 µg $kg^{-1}$ dw). Conversely, for IBU the slope of the RCF regression changed from 2.0 to 9.4 kg $kg^{-1}$ dw and from 0.20 to 0.94 kg $kg^{-1}$ dw for the LCF with initial or final soil concentrations, and Y-intercepts were negative. The slopes for the other compounds can be seen in Figure S1 (RCF) and S2 (LCF). All compounds showed good uptake into roots with RCF > 1 kg $kg^{-1}$ dw. Translocation to leaves was highest for CBZ and lowest for TCS. Most slopes increased when the final substrate concentration was used for the regression.

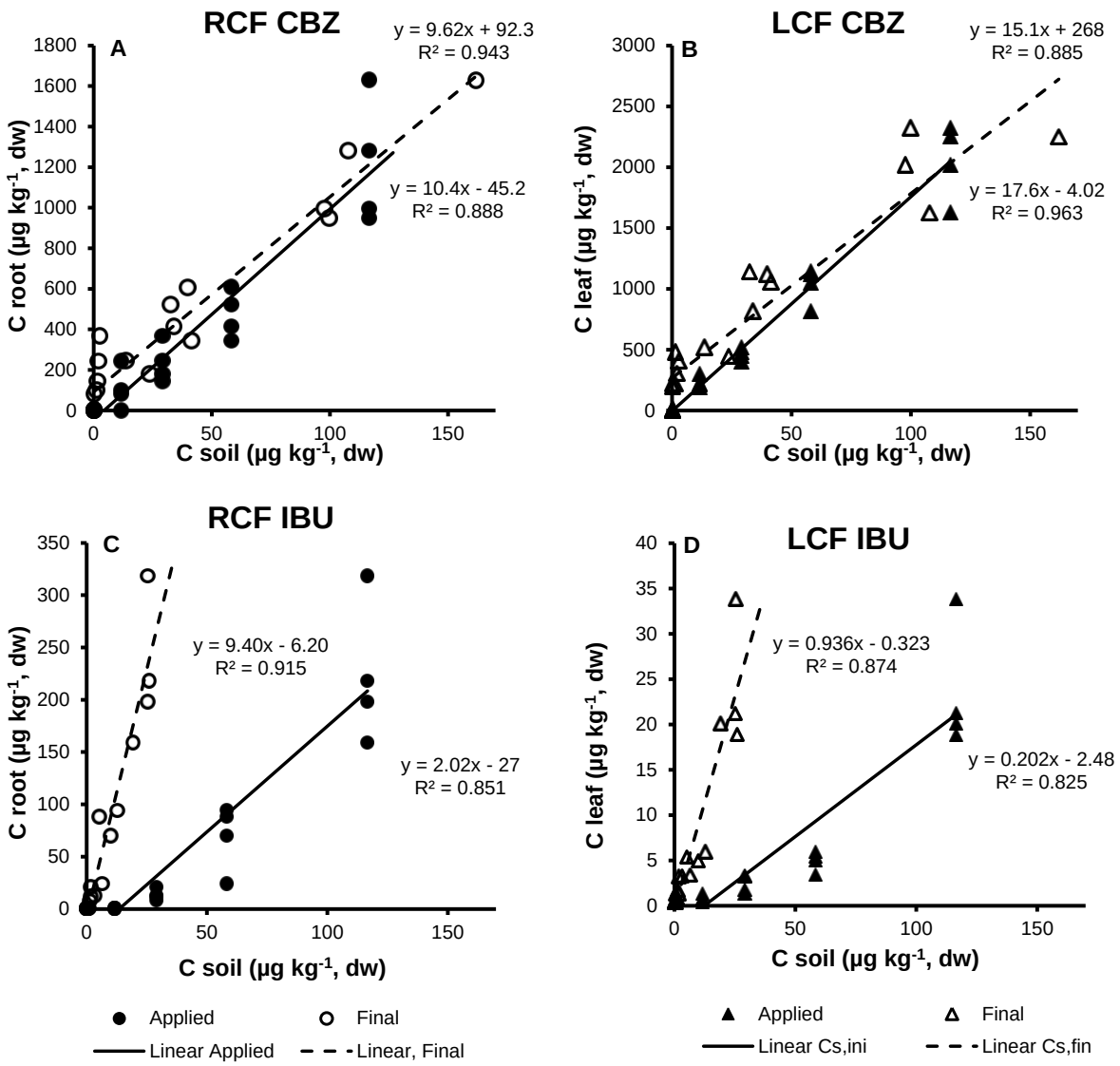


**Figure 1.** Root and leaf bioconcentration factors (RCFs and LCFs) of carbamazepine (CBZ) and ibuprofen (IBU). The solid and dashed lines represent the linear regression of the root and leaf concentration on the applied initial and the final soil concentration.

*Modeling*

The data obtained in the experiments (Table 2), such as dry weights at harvest and transpiration, were used to simulate plant uptake with the standard plant uptake model with degradation as described above (Eqs. 1-9). The loss rates from soil ($k_1$)

were calculated from the nominal initial concentration and the final measured concentration assuming exponential (1$^{st}$ order) decay (Table 3). Except one case (CAF, lowest applied amount), the loss rate from soil of all studied EOCs decreased when the initial concentration increased. For example, for CBZ the loss rates from soil were 0.090, 0.037, 0.015 and 0.006 $d^{-1}$ for the four treatments (11.7, 29.2, 58.3 and 116.7 µg $kg^{-1}$ dw). For IBU, the rates were 0.100, 0.094, 0.067 and 0.055 $d^{-1}$ for the same treatments.

Degradation rates in roots and leaves were determined by fitting simulated concentrations in plants to the measured ones. Figure 2 shows an example for the simulations with fit. The simulation of BPA succeeds without added degradation in roots or leaves, but only when dissipation from soil is considered. For CAF, on the other hand, the simulation improves when a fast degradation rate in leaves is assumed. The results of the linear model appear curved due to the changing degradation rates in soil. Judged from the correlation between calculated and average measured concentrations, the *Michaelis-Menten* kinetics in this case is closer to the measured result. In all cases, however, omitting degradation in soil (labeled as 00 in Fig. 2) leads to drastic overestimation. Fitted 1st-order dissipation rates of selected EOCs are shown in Table 3b. The fastest first-order dissipation rate from roots was fitted for CBZ (0.35 $d^{-1}$). Dissipation from roots also affects leaves, but nonetheless a rapid dissipation rate of CAF from leaves was required to meet the measured data. The adjusted parameters for the *Michaelis-Menten* kinetics in roots and leaves can be found in Table 3c. Fitted $v_{max}$ was higher in roots than in leaves, except for CAF. The values have to be taken with care

because the two parameters cannot be verified independently, but also because the fitted degradation must replace partly the missing dissipation from soil which, for mathematical reasons, could not be considered in the simulation with *Michaelis-Menten* kinetics.

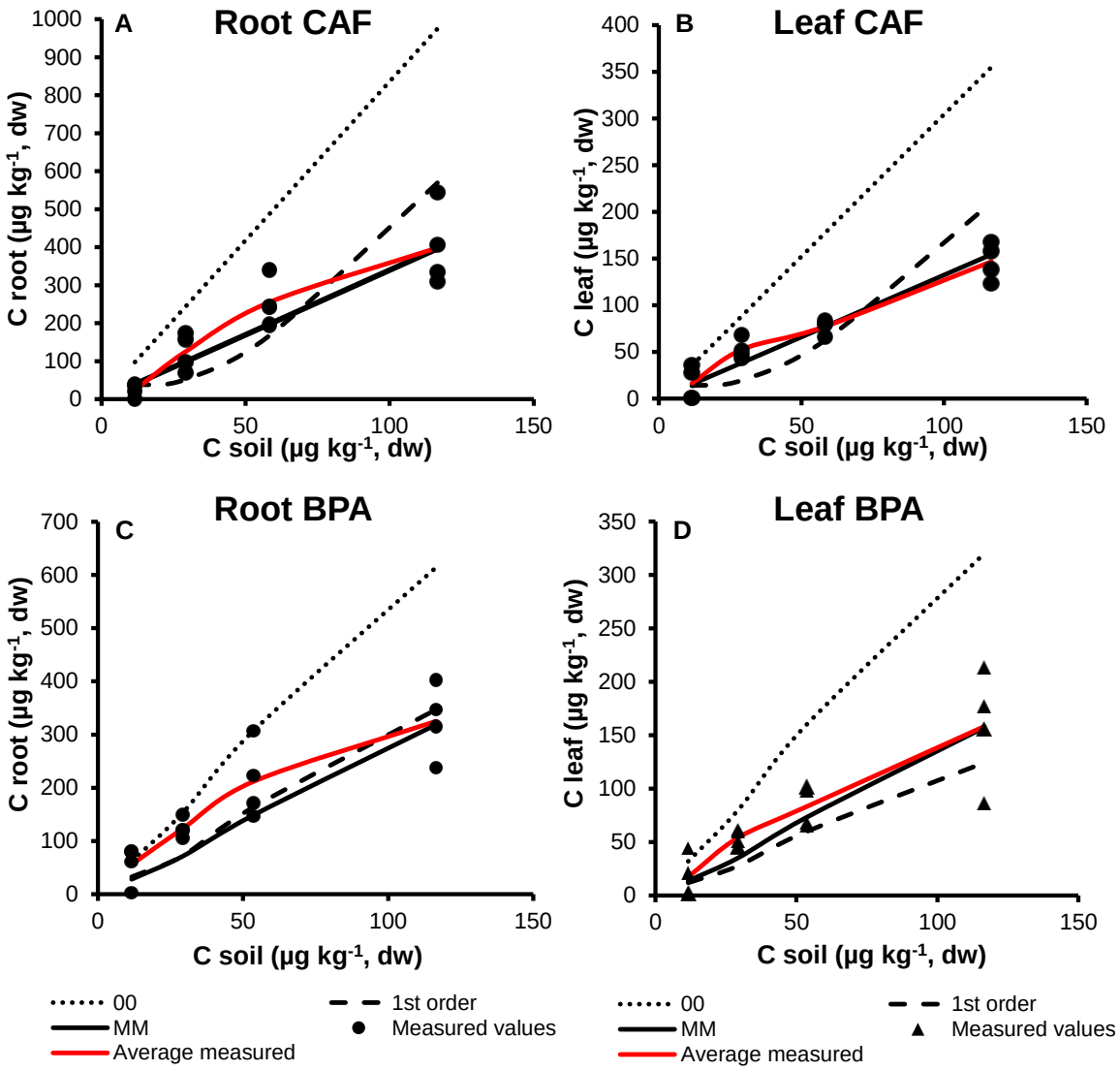


**Figure 2.** Simulated and measured concentrations in a) top left: CAF roots, b) top right: CAF leaves, c) bottom left: BPA roots; d) bottom right: BPA leaves. Solid points represent measured values; 00: no degradation in soil or plant; 1st: 1st order

288 degradation in soil, roots and leaves; MM: *Michaelis-Menten* degradation in roots
289 and leaves.

290 **Table 3a**. Calculated first order degradation rates in soil, $k_{soil}$, ($d^{-1}$) for the four
291 different treatments of selected EOCs (in brackets: standard deviation, n = 4).

| **Treatment (µg kg$^{-1}$ dw)** | **BPA** | **CAF** | **CBZ** | **IBU** | **PROP** | **TCS** |
|---|---|---|---|---|---|---|
| **11.7** | 0.039 (0.030) | 0.038 (0.008) | 0.109 (0.040) | 0.104 (0.010) | 0.088 (0.024) | 0.008 (0.010) |
| **29.2** | 0.038 (0.008) | 0.060 (0.004) | 0.058 (0.048) | 0.099 (0.013) | 0.080 (0.023) | 0.001 (0.012) |
| **58.3** | 0.031 (0.005) | 0.044 (0.012) | 0.017 (0.004) | 0.073 (0.015) | 0.076 (0.034) | 0.001 (0.020) |
| **116.7** | 0.029 (0.011) | 0.022 (0.006) | 0.001 (0.009) | 0.059 (0.005) | 0.063 (0.032) | 0.001 (0.008) |

292

293 **Table 3b.** Fitted first-order degradation rates in roots and leaves of selected EOCs.

| | **BPA** | **CAF** | **CBZ** | **TCS** |
|---|---|---|---|---|
| $k_{root}$ **(d$^{-1}$)** | 0.00 | 0.05 | 0.35 | 0.10 |
| $k_{leaf}$ **(d$^{-1}$)** | 0.00 | 1.50 | 0.05 | 0.00 |

294

295 **Table 3c.** Adjusted *Michaelis-Menten* parameters $v_{max}$ (mg kg$^{-1}$ d$^{-1}$) and $K_M$ (mg kg$^{-}$
296 $^{1}$) for enzymatic degradation in kinetics equation of selected EOCs.

| | **BPA** | **CAF** | **CBZ** | **TCS** |
|---|---|---|---|---|
| $v_{max}$ **root** | 0.01 | 6.0 | 0.20 | 0.20 |
| $K_M$ **root** | 0.10 | 5.0 | 0.45 | 1.00 |
| $v_{max}$ **leaf** | 0.0003 | 7.0 | 0.07 | 0.00 |
| $K_M$ **leaf** | 0.1 | 5.0 | 0.0001 | none |

297

298 **4. DISCUSSION**

299 *Bioconcentration factors*

300 Bioconcentration factors (BCF) are defined as concentration ratio between
301 organism and surrounding medium. However, the calculations can be done in
302 various ways. Some authors calculate BCFs from the concentration in the irrigation
303 water, others from the concentration in soil and some from the concentration in the
304 soil solution. Moreover, in some studies the nominal concentration is used while
305 others use the final concentration in soil at harvest to calculate the BCFs. In this
306 study, BCFs were derived as slope of the regression line so measurements at all
307 concentrations contributed simultaneously, without contribution of background (Y-
308 intercept), and with both initial (nominal) and final concentration (Figures SI1, SI2).
309 For CBZ there were no big differences in the BCF when it was calculated with
310 initial or final substrate concentration (Figure 1). On the other hand, for IBU the
311 difference was almost 5 times (2.0 to 9.4 g $g^{-1}$ dw). Thus, it is important to consider
312 that dissipation from soil or substrate will affect the BCF.

313 For most of the studied EOCs, experimental BCFs can be found in the literature
314 (Table 4). The reported values show large variance and are generally far higher in
315 hydroponics. In comparison to BCFs derived from experiments with soil, our values
316 are at the higher end, probably due to the lower adsorption capacity of perlite and
317 sand, compared to soil organic matter.

318 The half-lives (DT50) in the perlite and sand mixture are slower than those derived
319 in soil. The perlite and sand mixture was chosen as a substrate because in
320 laboratory studies we observed that there were lower interactions than when using

soil. The uptake simulations were done with measured $K_d$-values, thus, the difference in adsorption does not affect the simulations. But the substrate for this experiment lacked of organic matter, which can be used as main substrate by bacteria degrading co-metabolically EOC. This may explain why most loss rates from our substrate were lower than rates found in soil (Fent et al., 2003; Langdon et al., 2012; Matsumura et al., 2015). For example, DT50 of bisphenol A in soil have been determined from 0.5 to 7 days (Cousins et al., 2002, Ying et al., 2005 and Xu et al., 2009), while we found half-lives from 17.8 to 23.9 days. BPA dissipation is related to bacteria in soil and it dissipates faster in more aerobic environments (Fent et al., 2003).

**Table 4.** Experimental values of bioconcentration factors and dissipation times in soils reported and in this study.

| EOC | Experiment Type | Plant | Tissue | BCF literature | BCF in this study (kg $kg^{-1}$ dw) | DT50 (d) in literature | DT50 (d) this study |
|---|---|---|---|---|---|---|---|
| BPA | Hydroponics | Dracaena[a] | Stem | 170 L $kg^{-1}$ dw | Leaf 1.3 – 2.7<br>Root 2.6 – 4.5 | 0.5 – 7[i,j,k] | 17.8 - 23.9 |
| | | | Root | 110 L $kg^{-1}$ dw | | | |
| | | Lettuce, collard[b] | Leaf | 7 - 66 L $kg^{-1}$ dw | | | |
| | | | Root | 4339 - 9587 L $kg^{-1}$ | | | |
| CAF | Soil | Cucumber, tomato, sweet potato, carrot[c,d] | Leaf | 0.4 – 17 L $kg^{-1}$ dw | Leaf 1.2 – 0.94<br>Root 3.5 – 5.3 | 1.5 – 3[l,m] | 11.6 - 31.5 |
| | | Cucumber, tomato[c] | Fruit | 0.4 – 5.3 L $kg^{-1}$ dw | | | |
| | | Sweet potato, carrot[d] | Root | 0.1 – 0.8 kg $kg^{-1}$ dw | | | |
| CBZ | Soil | Soybean, radish, cucumber, tomato, sweet potato[c,d,e,f] | Leaf | 0.6 - 425 kg $kg^{-1}$ dw | Leaf 15 – 17.6<br>Root 9.9 – 10.4 | 60 – 533[n,o] | 6.4 - 693 |
| | | Soybean, radish, sweet potato, carrot[d,e,f] | Root | 0.1 – 8.3 kg $kg^{-1}$ dw | | | |
| | | Cucumber, tomato[c] | Fruit | 0.4 - 27 kg $kg^{-1}$ dw | | | |
| IBU | Hydroponics | Typha, phragmites, iris, juncus[g] | Root | 7 – 201 L $kg^{-1}$ | Leaf 0.2 – 0.94<br>Root 2.0 – 9.4 | 1 – 6[i,p] | 6.7 - 11.7 |
| PROP | Soil | Radish, ryegrass[f] | Leaf<br>Root<br>Root | 0.01 – 11.9 kg $kg^{-1}$ dw<br>1.2 kg $kg^{-1}$ dw<br>1.2 kg $kg^{-1}$ dw | Leaf 1.1 – 2.9<br>Root 3.2 – 6.7 | > 40[f] | 7.9 - 11 |
| TCS | Soil | Radish, ryegrass[f] | Leaf | 0.1 - 38 kg $kg^{-1}$ dw | Leaf 0.15 – 0.24<br>Root 4.4 – 6.9 | 18 – 187[q,r,s] | 86.6 - 693 |
| | | | Root | 0.12 kg $kg^{-1}$ dw | | | |
| TON | Soil | Carrot | Leaf | 0.18 kg $kg^{-1}$ dw | Leaf 2.7 – 5.9dw<br>Root 5.3 – 12 kg $kg^{-1}$ dw | 50 – 133[s] | |
| | | Carrot, barley, meadow | Root | 0.50 – 2.74 kg $kg^{-1}$ dw | | | |

[a]Saiyood et al. (2010), [b]Dodgen et al. (2013), [c]Goldstein et al. (2014), [d]Malchi et al. (2014), [e]Wu et al. (2010), [f]Carter et al. (2014), [g]Zhang et al. (2016), [h]Macherius et al. (2012), [i]Xu et al. (2009), [j]Cousins et al. (2002), [k]Ying et al. (2005), [l]Lin et al. (2010), [m]Hendel et al. (2006), [n]Monteiro et al. (2009), [o]Walters et al. (2010), [p]Löffler et al. (2005), [q]Ying et al. (2007), [r]Walters et al. (2010), [s]Chen et al. (2014).

336

337 *Degradation*

338 Dissipation rates from soil in Table 3a were calculated from initial nominal and final
339 measured substance concentrations in the substrate. Rates decreased with
340 increasing concentrations. Such kinetics, i.e. decreasing (pseudo) first-order rates
341 with increasing substrate concentrations, can occur by enzymatic degradation
342 when the half-saturation concentration $K_M$ of the reaction is within the range of
343 occurring concentrations and when at the same time the amount of enzymes is
344 constant. Thus, co-metabolic (non-growth) degradation by microbes living in the
345 substrate or near and in the roots, but also degradation by roots itself can lead to
346 this kinetics. At higher soil concentrations, PROP, IBU, BPA and CAF had the
347 highest dissipation rates, while CBZ and TCS showed the lowest dissipation. As it
348 can be seen in Table 4, several studies suggest that CBZ is relative persistent with
349 half-lives in soil (DT50) over 60 days. Moreover, TCS and its metabolites were
350 found in soil still four years after the application with biosolids (Macherius et al.,
351 2014). The other compounds are more labile to degradation. For example,
352 metabolites of BPA have been found in soil such as 4-hydroxyacetophenone, 4-
353 hydroxybenzaldehyde and 4-hydroxybenzoic acid (Dodgen et al., 2014). Hurtado et
354 al. (2016) determined the concentrations of test chemicals both in the bulk soil, and
355 in the vicinity of roots. Only TCS showed an enrichment in the soil around roots,
356 underlining its persistence. Low concentrations in the soil near roots were found for
357 PROP and IBU, which also had the highest loss rates from soil (Table 3a). This

makes it likely that degradation is enhanced by roots. Furthermore, enantiomeric fractionation of IBU was observed, with an enrichment of the *S*-enantiomer.

*Inverse modeling*

Inverse modeling can be a powerful tool to determine missing processes or rate constants and is often used for model calibration. Jacobsen et al. (2015) used the technique to find missing *in-planta*-degradation of pesticides, and the principle applied here is similar: model predictions are compared to measured concentrations, and the difference is contributed to dissipation by degradation. This method is of course highly uncertain because both model simulation and experiment have their own uncertainties, and unknown dissipation processes can lead to reduced uptake. It is therefore a positive sign that the model in no case underestimated the experimental concentrations, and that often only a rather small dissipation rate was sufficient (Table 3).

Two degradation kinetics were evaluated: first-order kinetics and *Michaelis-Menten*. It is noteworthy to mention that the first-order kinetic has only one parameter to adjust ($k$) while *Michaelis-Menten* has two ($v_{max}$ and $K_M$). Moreover, mathematical constraints did not allow considering the (known) dissipation from soil. The first-order fit is therefore preferable in our case.

Measured root and leaf concentrations of BPA were very close to those predicted, thus, no degradation rates were fitted (Table 3b). We did not find degradation studies of BPA in plants for comparison. A large difference between predicted CAF concentrations in leaves and measured values required to fit the $k_{leaf}$ to 1.50 $d^{-1}$.

Dettenmaier et al. (2009) derived the transpiration stream concentration factor (TSCF) with a pressure chamber experiment of several organic compounds and reported that polar neutral compounds such as CAF should be taken up rapidly by roots and translocated to the leaves. On the other hand, Goldstein et al. (2014) and Wu et al. (2014) reported that CAF was translocated to leaves less than CBZ due to polar interactions. In the experiments of Hurtado et al. (2016), similar behavior was observed, and the concentrations predicted for leaves were far above the measured ones. Both phenomenon reduced translocation or rapid transformation of CAF in leaves can lead to this discrepancy. In the literature, no degradation rates have been reported for CAF in plants. Regarding CBZ, transformation products (TPs) have been reported both for soil and plants, such as 10,11-epoxy carbamazepine, 10,11-dihydroxycarbamazepine or 10,11-dihydro-10,11-dihydroxy-carbamazepine (Goldstein et al., 2014; Malchi et al., 2014). Malchi et al. (2014) reported that in soil, CBZ parent compound was dominant (90%) and in leaves it depended on the species (potato or carrot). Goldstein et al. (2014) reported similar TPs and similar percentages in cucumbers and tomatoes. Metabolites formed in soil can also be taken up by plants, which makes it difficult to differentiate where exactly the degradation occurred.

Recently, Pietrini et al. (2015) detected 11 TPs of IBU in *Lemna gibba* L. plant extracts when plants were exposed to 1 mg $L^{-1}$ of IBU. In microalgae reactors, IBU and CAF were rapidly biodegraded (Matamoros et al. 2016), while CBZ appeared to be recalcitrant. In this case, the *S*-enantiomer of IBU was degraded faster. TCS was metabolized in carrot and horseradish to conjugates, and the final amount of

403 conjugates was five times higher than that of TCS (Macherius et al., 2012b). With
404 the fitted degradation rate in roots of 0.1 $d^{-1}$, such a ratio would be reached after 18
405 days, it is thus reasonable. In horseradish, 33 metabolites of TCS were detected,
406 hereof 23 identified (Macherius et al., 2014)

407

408 **CONCLUSIONS**

409 Biodegradation of emerging contaminants in plants has been observed in many
410 cases but kinetics data are rare. Inverse modeling may provide a way to obtain this
411 missing information. Rates determined by inverse modeling are, despite the
412 inherent uncertainty, indicative of the dissipation rates. In the present study,
413 degradation kinetics was in the order BPA < CAF ≈ TCS < CBZ for roots, and BPA
414 = TCS < CBZ << CAF for leaves. There are indications that the high rate for CAF
415 could also compensate for less translocation than predicted.

416 In soil, decreasing first-order dissipation rates with increasing concentration were
417 observed. Co-metabolic degradation can explain this kinetics. The dissipation rates
418 were in the order TCS < BPA ≈ CAF < PROP ≈ IBU ≈ CBZ for the lowest initial
419 concentration, and TCS ≈ CBZ < CAF ≈ BPA < IBU ≈ PROP at the highest applied
420 dose.

421 The shape of the BCF-curve (the ratio of concentration in plant to soil) and the Y-
422 intercept gives information on the type of degradation kinetics. A negative Y-
423 intercept can be obtained from (rapid) enzymatic degradation in plants. Finally, the
424 use of inverse modeling provides additional knowledge in the biodegradation of

chemicals that can be taken up and further translocated in plants. This can be very helpful to assess where biodegradation takes places and this method can be used to study further metabolism in plant.

Dissipation kinetics found via inverse modeling is not a conclusive proof for biodegradation and confirmation by experimental studies (for example, by determination of metabolites or by studies with labeled compounds) is needed.

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607

608 **Figure Captions**

609 **Figure 1.** Root and leaf bioconcentration factors (RCFs and LCFs) of
610 carbamazepine (CBZ) and ibuprofen (IBU). The solid and dashed lines represent
611 the linear regression of the root and leaf concentration on the applied initial and the
612 final soil concentration.

613

614 **Figure 2.** Simulated and measured concentrations in a) top left: CAF roots, b) top
615 right: CAF leaves, c) bottom left: BPA roots; d) bottom right: BPA leaves. Solid
616 points represent measured values; 00: no degradation in soil or plant; 1st: 1st order
617 degradation in soil, roots and leaves; MM: *Michaelis-Menten* degradation in roots
618 and leaves.

619

620